

METHOD 25A - DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

Applicability

This method is applicable for the determination of total gaseous organic concentration of vapors, **including methane**, consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The emissions are **expressed in terms of methane** unless the permit states otherwise.

Summary of Method

A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas. If the calibration gases are not methane, results will be corrected to a methane basis by use of a response factor, unless the permit limit states a basis other than methane.

Apparatus

Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. All sampling components leading to the analyzer will be heated $\geq 110^{\circ}\text{EC}$ (220°EF) throughout the sampling period, unless safety reasons are cited.

Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block will be heated $>120^{\circ}\text{EC}$ (250°EF).

Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes will be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

Heated Sample Line. Stainless steel or Teflon® tubing to transport the sample gas to the analyzer. The sample line should be heated ($\geq 110^{\circ}\text{EC}$) to prevent any condensation.

Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are acceptable.

Particulate Filter. An in-stack or an out-of-stack glass fiber filter is required except as explained and justified in the Proposed Deviation from the Method Section. An out-of-stack filter should be heated to prevent any condensation.

Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

Analytical Range

The span value should be between 1.5 to 2.5 times the applicable in-stack concentration based on the emission limit.

Allowable = _____ lb/hr

MW = _____ lb/lbmole

Stack Flow = _____ scfm

The in-stack concentration based on the emission standard and stack flow parameters is

$\frac{(\text{lb/hr}) \times (387 \times 10^6)}{(\text{MW}) \times (\text{scfm}) \times 60} = \text{_____ ppm.}$ Therefore, the analyzer span will be _____ ppm.

Calibration Gases

The calibration gases for the gas analyzer will be methane in air or methane in nitrogen.

Alternatively, organic compounds other than methane can be used; the appropriate corrections for response factor must be made. The calibration gases will be _____.

Calibration gases will be EPA Protocol No. 1 gases and will include a recommended shelf-life from the manufacturer over which the concentration does not change more than $\pm 2\%$ from the certified value.

Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (methane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value. The low-level gas to be used during the source test will be _____.

Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value. The mid-level gas to be used during the source test will be _____.

High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value. The high-level gas to be used during the source test will be _____.

Analyzer Calibration

The calibration procedures described in Method 6C (calibration error, bias and drift) will be followed unless deemed not feasible and approved by the on-site BTS observer.

The analyzer calibration error check will be conducted by introducing the zero, low-range, mid-range, and high-range gases to the analyzer. During this check, no adjustments to the system will be made except those necessary to achieve the correct calibration gas flow rate at the

analyzer. The analyzer responses to each calibration gas will be recorded. The analyzer calibration error check will be considered invalid if the gas concentration displayed by the analyzer exceeds ± 2 percent of the span for any of the calibration gases.

The sampling system bias check will be performed by introducing first an upscale gas (mid-range) at the calibration valve assembly installed at the outlet of the sampling probe, and then the zero gas. During this check, no adjustments to the system will be made except those necessary to achieve the correct calibration gas flow at the analyzer. This check will be considered invalid if the difference between the calibration error check and the calibration bias check for the same calibration gas exceeds $\pm 5\%$ of the span.

Alternatively, **if approved by the BTS observer**, the following calibration error test will be performed. Immediately prior to the test series (within 2 hours of the start of the test), zero gas and high-level calibration gas will be introduced at the calibration valve assembly. The analyzer output will be adjusted to the appropriate levels, if necessary. The predicted response will be calculated for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then the low-level and mid-level calibration gases will be introduced successively to the measurement system. The analyzer responses will be recorded for low-level and mid-level calibration gases and the differences between the measurement system responses and the predicted responses determined. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and will be replaced or repaired prior to testing. No adjustments to the measurement system will be made after the calibration and before the drift check. If adjustments are necessary before the completion of the test series, drift checks will be performed prior to the required adjustments and the calibration following the adjustments repeated. If multiple electronic ranges are to be used, each additional range will be checked with a mid-level calibration gas to verify the multiplication factor.

Response Time Test. Zero gas will be introduced into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. The time will be recorded from the concentration change to the measurement system response equivalent to 95 percent of the step change. The test will be repeated three times and the results averaged.

Emission Measurement Test Procedure

Organic Measurement. Sampling will begin at the start of the test period at a sample point that is centrally located in the stack. The time and any required process information will be recorded, as appropriate, in particular, noting on the recording chart, periods of process interruption or cyclic operation.

Bias and Drift Determination. Immediately following the completion of the test period and hourly during the test period, the zero and mid-level calibration gases will be re-introduced one at a time to the measurement system at the calibration valve assembly. No adjustments to the measurement system will be made until both the zero and calibration bias and drift checks are made. The analyzer response will be recorded. If the bias values exceed the specified limits, the test results preceding the check will be invalidated and the test will be repeated following

corrections to the measurement system and full recalibration. If the drift values exceed the specified limits, the run may be accepted but the test measurement system will be fully recalibrated and the results reported using Method 6C correction. If the alternative calibration error test was approved, both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

Measurement System Performance Specifications

Zero Drift, less than or equal to ± 3 percent of the span value. **Calibration Drift**, less than or equal to ± 3 percent of span value. **Calibration Error**, less than or equal to ± 2 percent of span for Method 6C procedures, less than or equal to ± 5 percent of the calibration gas value for the alternative procedures. **Sampling System Bias**, less than or equal to ± 5 percent of the calibration gas value for Method 6C procedures.

Emission Calculation

Calculations will be done per the method including Method 6C (Equation 6C-1) drift corrections. Emissions will be presented in the following units: _____.

Proposed Deviations from this BTS Template or the Method

(Insert any proposed deviations here)